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# METHOD OF PHOTOCHEMICALLY REMOVING AMMONIA FROM GAS STREAMS

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# METHOD OF PHOTOCHEMICALLY REMOVING AMMONIA FROM GAS STREAMS

## CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of United States patent application serial no. 10/269,204 filed October 11, 2002 which was a continuation-in-part of United States patent application serial no. 09/847,476 filed May 2, 2001 and United States patent application serial no. 10/098,759 filed March 14, 2002.

## FIELD OF THE INVENTION

Photochemically initiated free radical reactions involving nitrogen oxides ($NO_x$), carbon monoxide (CO) , hydrocarbons, and water vapor are used to oxidize ammonia gas in the effluent gas streams leaving nitrogen oxides control systems. It is known that selective catalytic reduction (SCR) systems and selective noncatalytic reduction (SNCR) systems generate limited quantities of ammonia gas. The ability to control nitrogen oxides by SCR and SNCR systems is often limited by the need to avoid high concentrations of ammonia and by the formation of ammonium compounds that can accumulate on industrial heat exchange equipment and air pollution control systems. The process disclosed herein is typically installed downstream from nitrogen oxides control equipment used on coal, oil, and natural gas-fired boilers and cement kilns. The photochemically free radical reactions result in the oxidative destruction of the ammonia.

## BACKGROUND OF THE INVENTION

The control of nitrogen oxides (primarily nitric oxide, NO, and nitrogen dioxide, $NO_2$) is an important national goal. Nitrogen oxide emissions contribute to the formation of smog, fine particulate matter (often termed PM2.5), and regional haze. Nitrogen oxides also participate in the atmospheric reactions that lead to the formation of acid rain. To control nitrogen oxides, the Clean Air Act includes numerous significant requirements that apply to stationary sources such as fossil-fuel fired boilers, wood waste fired boilers, municipal waste incinerators, medical waste incinerators, cement kilns, and other industrial processes. Industrial sources are presently applying a variety of nitrogen oxides control techniques either alone or as combinations of systems to achieve the $NO_x$ control limitations that become effective in the near future.

Selective noncatalytic reduction (SNCR) systems can be installed on a variety of fossil fuel and waste fuel fired combustion systems and on cement kilns. SNCR systems inject either ammonia or urea reagent into the combustion gas stream at a point in the combustion or kiln process where the gas temperature is in the range of 1600°F to 2000°F. In this temperature range, the ammonia or urea reagents react with the $NO_x$ compounds, which are then chemically reduced to harmless diatomic nitrogen, $N_2$. Due to the limitations of reagent mixing in the gas stream and the limited residence time of the gas stream in the critical temperature range, a portion of the ammonia and urea reagents fails to react. Ammonia gas is emitted from both ammonia and urea based SNCR systems. These emissions are termed ammonia "slip" and are usually in the range of 2 ppm to 40 ppm. To minimize ammonia emissions, operators of SNCR systems must often reduce the quantity of ammonia or urea reagent injected

(stoichiometric ratio of reagent to $NO_x$) into the system and, thereby, also reduce the overall extent of $NO_x$ emission reduction. The limits of $NO_x$ reduction efficiency of SNCR systems due to ammonia slip related problems are described in technical papers by Hurst & White (361), Jones (961), Quartacy et al. (250), Moilanen et al (576), Gullett et al (597), Pachy et al. (598), and Sun et al. (956).

Selective catalytic reduction (SCR) systems use a vanadium pentoxide-titanium dioxide-tungsten oxide or zeolite catalyst bed mounted in a portion of the combustion system effluent gas stream that is at temperatures of 500°F to 1000°F. Ammonia reagent is injected into the combustion gas stream before it reaches the catalyst bed. In the presence of the catalyst, the ammonia chemically reduces the nitrogen oxides. SCR systems can achieve high NOx reduction efficiencies when stoichiometric levels of ammonia reagent are used; however, some of the ammonia can penetrate the SCR system. SCR system operators must often reduce the rate of ammonia injection in order to avoid undesirable levels of ammonia slip. This reduces the NOx control efficiency of the SCR system. The ammonia slip imposed limitation to the performance of SCR systems is described further in technical papers by Donnelly et al. (88), Durilla et al. (1170), Buschmann et al. (116), The U.S. Department of Energy (978), and Gullett (597).

In addition to SNCR systems and SCR systems, operators of fossil fuel-fired boilers, waste-fired incinerators, and cement kilns often use modified combustion system operating conditions, low $NO_x$ burners, and gas reburning systems to suppress NOx concentrations before the gas streams to be treated reach the SNCR and/or SCR

equipment. When these $NO_x$ concentration suppression techniques are used to their maximum design limits, additional organic compounds are formed and remain in the gas stream. The process disclosed here benefits from the presence of these organic compounds, which serve as participants in the free radical chain reactions used to destroy ammonia gas.

Available ammonia control techniques are not well suited for the control of ammonia gas emissions from $NO_x$ control systems. Ammonia scrubbers, such as those used in some chemical industry sources, use packed bed, tray tower, and spray tower absorbers. All of these scrubbers are designed for ammonia gas concentrations substantially higher than the concentrations generated by SNCR and SCR systems operating at or near their design limits. These conventional ammonia wet scrubbers have poor efficiencies for gas streams having low ammonia gas concentrations. Furthermore, the wet scrubbers require large vessels and liquid handling systems and, thereby, cannot be retrofitted into many existing boiler stations having limited space. The liquid streams from the scrubbers must be treated to prevent contaminant releases to surface waterways or the groundwater.

Conventional ammonia scrubbers do not provide an economically feasible and practical means to control ammonia emissions from $NO_x$ systems.

Photochemical destruction of volatile organic compounds (VOCs) is known. U.S. Patent No. 3,977,952 discloses a process for the decomposition of one or more carbon-containing compounds such as in an industrial waste or flue gas containing volatile

organic compounds, oxygen, and water vapor. The method is carried out by exposing humidified gas to radiation of a wavelength of about 20 to 600 nanometers.

In some industrial processes, such as pyroprocessing of cement, recovery of the particulate matter solids produces material that is of economic importance. A discussion of dry sorption methods is found in U.S. Pat. No. 6,080,281 teaching an emission control process using photocatalytic and nonphotocatalytic aerogels for adsorption, and exposing the photocatalytic aerogel material containing adsorbed VOCs to ultraviolet (UV) radiation resulting in VOC destruction.

U.S. Patent No. 4,210,503 discloses a direct photolysis method for controlling gaseous emissions, particularly vinyl chloride, by exposing the emissions to UV light and, thereafter, absorbing such decomposition products in a scrubber that substantially eliminates the vinyl chloride and most other decomposition products from the effluent stream.

U.S. Patent No. 4,981,650 discloses a method to remove dioxin-contaminated waste by extraction in a liquid capable of extracting dioxins. A hydrogen donor is added to the extracting solvent or later during addition of an activating agent. The dioxin-containing liquid extract is treated in a direct photolysis reactor that contains immersion UV lamps.

U.S Patent No. 5,045,288 discloses the removal of halogenated and non-halogenated volatile and non-volatile organic contaminants from a gaseous stream by mixing a gaseous oxygen bearing substance with the contaminated gaseous stream, contacting the mixture with a solid photocatalyst, and exposing the photocatalyst and

organic components to UV light having a wavelength up to 600 nanometers. The catalyst is pre-selected to prevent formation of a liquid phase.

U.S. Patent No. 5,417,825 discloses a thermal photolytic process that uses high temperatures in combination with radiation exposure to induce a photochemical reaction to detoxify a wide variety of organic pollutants, for example, chlorinated aromatic hydrocarbons. The hydrocarbons are treated in the gaseous phase by heating the gas to a temperature greater than 200°C, preferably 600°C to 800°C, and exposing the heated gas to radiation at wavelengths of less than 280 nanometers, preferably from 185 nanometers to 280 nanometers, for at least two seconds.

U.S. Patent No. 5,650,549 teaches a photothermal process for the detoxification of chlorinated aromatic hydrocarbons contained in a gas stream. The chlorinated aromatic hydrocarbons are heated to a temperature of greater than 200°C to form a gas stream, or a pre-existing chlorinated aromatic hydrocarbon containing gas stream is produced from a combustion source at a temperature of greater than 200°C. The gas stream is exposed to radiation at a wavelength of less than 280 nanometers for at least one second to convert the chlorinated aromatic hydrocarbons nontoxic reaction products, and the gas stream is released to the atmosphere.

U.S. Patent No. 5,839,078 discloses a method of direct vitrification of nuclear waste comprising the steps of providing waste in the form of relatively small pieces with vitrifiable material, providing a high intensity light source of sufficient power to cause melting and subsequent vitrification of said waste, and cooling and storing of said vitrified material.

U.S. Patent No. 5,342,582 discloses an apparatus for reprocessing special wastes of photopolymerizable scrap material to produce domestic waste, comprising a housing equipped with a feed hopper, at least one UV emitter arranged in the housing to irradiate and heat the scrap material, and a chopper arranged in the housing to comminute the scrap material. The photocrosslinkable and thermally crosslinkable scrap is composed of, for example, dry resist, solder resist, color proof films, screen printing films, and the like, which form special waste because of their reactive constituents.

U.S. Patent No. 5,476,975 discloses a method for photodegradation of a solution of organic toxic chemicals recoverable from contaminated wood products by the use of a super-critical fluid by exposing the extracted solution to UV in the presence of a photosensitizer.

U.S. Patent No. 5,935,525 discloses a pre-treatment system and an air treatment system for abatement of contaminated air that includes pollutants such as VOCs, $NO_x$, and/or carbon monoxide (CO). The air stream is treated using UV light under conditions that produce hydroxyls, peroxides, and other oxidants without the formation of ozone. These oxidants are also used in the activated air with activated water being formed as an aqueous solution (vapor) of the activated air. The pre-treatment system includes a quenching zone where activated water is misted into the air stream, followed by alternating reaction zones and depletion zones where activated air is added and then turbulently mixed with the air stream. The air treatment system includes a primary treatment tunnel, a carbon bed system, an activated air generator, and a sparger tank farm. Activated air produced by the generator is added to water while being exposed to

UV light in the sparger tank farm. As the contaminated air stream moves through various sequential chambers within the tunnel, it is subjected to the misted activated water while being simultaneously exposed to UV radiation. Air exiting the tunnel is then further treated in the carbon bed system.

U.S. Patent No. 6,179,971 discloses a two-step process for air purification comprising a photolytic step followed by a photocatalytic step, each of which entails radiation treatment to convert contaminants into less harmful products. The method provides a photolytic stage having a source of UV radiation and a downstream photocatalytic stage using a photocatalyst and a source of UV radiation.

U.S. Patent No. 5,538,537 discloses a method of desulfurizing furnace flue gases laden with sulfur dioxide ($SO_2$) comprising cooling the flue gases to a temperature near but above the dew point thereof and flowing the cooled flue gases through a bed of granular cement stone sorbent prepared from a mixture of cement and water. The sorbent laden with pollutants from the flue gases can be further processed directly in an advantageous manner in a cement plant, for example, by grinding it together with cement clinker or separately therefrom and thereby adding it as a component, for example as a gypsum component, to a cement that is to be produced, so that no disposal problems exist for the sorbent laden with pollutants. With the addition of ashes or fly ashes from coal or fluosolids furnaces, a particularly environmentally friendly means for disposal of these ashes can be achieved simultaneously if a sorbent laden with pollutants from the flue gases is further processed for the production of cement (together with cement clinker). Sorbent is produced. It is advantageous to use it with a grain size of greater than 1 mm, preferably approximately 4 to 20 mm. A mixture of

granulated cement stone and carbonaceous sorption material then forms the sorbent used according to the invention, which is brought into contact with flue gases that are to be purified.

U.S. Patent No. 4,634,583 discloses a method for the desulfurization of a calcium-containing flue gas stream from a firing system such as a cement-making plant wherein at least partially deacidified, hot, raw cement meal is added to the flue gas at selected points to adsorb the sulfur oxides onto the calcium present in the gas. No additional adsorption agents, for example, activated carbon, pure calcium oxide, milk of lime, or the like are used. Raw cement meal having an adequately high proportion of free calcium oxide is conveyed to the conduit of the exhaust gas to be desulfurized. The preferred method comprises suspending the deacidified raw cement meal in the flue gas in the form of a cloud of airborne dust and, thereafter, separating the dust from the flue gas after the sulfur oxides have been bonded to the calcium.

U.S. Patent No. 5,137,704 discloses a process for decreasing the $NO_x$ content of exhaust gases from cement-burning kilns by an addition of ammonia and/or ammonia-containing substances to the hot exhaust gases. The exhaust gases are desulfurized at a temperature from 50°C to 100°C in a dry or semidry process by a mixture of raw cement powder and calcium hydroxide. The mixed solids that have been removed from the exhaust gas in a dry state in the desulfurizing stage are returned to the exhaust gas stream at temperatures from 850°C to 1,000°C.

Treatment methods for pollutant-bearing gas in a corona discharge device is a known method of removing the pollutants. A general review of this technique is provided in Puchkarev et al., "Toxic Gas Decomposition by Surface Discharge,"

Proceedings of the 1994 International Conf. on Plasma Science, Jun. 6-8, 1994, Santa Fe, N.M., paper No. 1E6, page 88. Corona discharge systems used for removal of mercury are disclosed in U.S. Patent No. 5,591,412.

Injection of activated carbon in waste gas effluent is known. See U.S. Patents Nos. 4,196,173; 4,889,698; 5,053,209; 5,607,496; and 5,672,323.

## SUMMARY OF THE INVENTION

In a basic aspect, the invention provides a photochemically initiated set of free radical reactions involving nitrogen oxides, carbon monoxide, hydrocarbons, water vapor, and ammonia that result in the oxidation of ammonia gas in the effluent gas stream of an industrial process. It is desirable to prevent the formation of undesirable byproducts, therefore, the light intensity and/or the time exposed to UV irradiation are limited to ensure that the conversion of NO to $NO_2$ is not complete and that the sum of NO and $NO_2$ (termed $NO_x$) is not substantially reduced . In a preferred process it is desirable that the initial $NO_x$ concentration not be reduced by more than 50%. The treated gases are released directly to the atmosphere after treatment.

In one embodiment, the present invention involves irradiation of an ammonia-containing gas stream within the last stage of an SCR catalyst bed and/or on the process gas side of boiler air preheaters. The reactions initiated in the hot, particulate matter-laden gas stream result in the destruction of ammonia gas before it can react with sulfuric acid and other sulfur-containing gases to form sticky deposits of ammonium bisulfate and/or ammonium sulfate. The irradiation employed is ultraviolet light. The treatment of ammonia with radiation in accordance with the invention is especially

efficient when employing UV sources that emit light in the spectral range of 230 to 370 nanometers under conditions typically encountered in industrial effluent gas streams containing less than 50 ppm of ammonia. The radiation of the ammonia gas stream results in the rapid and efficient direct photolytic destruction of ammonia due to free radical related hydrogen abstraction from the ammonia molecule prior to release of the effluent gas stream to the atmosphere. The process leads to the formation of diatomic nitrogen, $N_2$.

In another embodiment, the present invention involves irradiation of an ammonia-containing gas stream within the last stage of an SCR catalyst bed and/or on the process gas side of boiler air preheaters using ultraviolet light having wavelengths between 230 nanometers to 370 nanometers.

Further, the present invention entails a method for treating an industrial production process that emits a gaseous effluent stream containing ammonia, and comprises the following:

a) oxidizing ammonia in the industrial effluent gas stream by direct photochemical oxidation in the absence of added photocatalyst by irradiating the gas stream with UV light after removal of particulate matter

b) oxidizing ammonia in the industrial effluent gas stream by direct photochemical oxidation in the absence of added photocatalyst by irradiating the gas stream with UV light prior to the removal of particulate matter while the industrial gas stream is passing through the last stage of the SCR catalyst bed

Various specific and/or preferred aspects are specified herein below, and other objects and advantages of the present invention will become apparent and obvious from a study of the following description and the accompanying drawings that are merely illustrative of such invention.

## BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic illustration of the ammonia destruction process of the present invention illustrating the removal of ammonia gas from an the effluent gas stream of an industrial process having either an SCR and/or SNCR $NO_x$ control system.

Figure 2 is a schematic illustration of the application of the ammonia destruction process for the removal of ammonia from a cement kiln effluent gas stream formed due to the volatilization of nitrogeneous material in the raw kiln feed entering the kiln pyroprocessing system in a counterflow direction.

Figure 3 illustrates concentration profiles for free radical chain reactions initiated in a gas mixture of $NO_x$, CO, hydrocarbons and water vapor.

## DETAILED DESCRIPTION OF THE INVENTION

The ammonia destruction process is applicable to a number of industrial processes, such as coal, oil, and natural gas-fired boilers, wood-fired boilers, waste-fired incinerators, and portland cement plants. In the case of cement plants, the present invention entails irradiating the effluent gas stream that passes from a pyroprocessing system of the cement plant. In this regard, the gas streams are treated in Stage I and

Stage II controls with nonphotocatalyzed direct photolysis using irradiated UV light in the spectral range of 230 to 370 nanometers. Stage I control occurs in a particulate matter-laden gas stream located close to the location of ammonia gas generation in the industrial process stream and is intended to protect downstream equipment from corrosive and sticky ammonium compounds. Stage II control is performed in a gas stream that has been treated in a high efficiency particulate matter control system to reduce the particulate matter concentrations by a factor of 95% to 99.9%. Stage II control is performed to minimize the release of ammonia gas to the atmosphere.

Particulate matter control devices coupled to irradiation sources employed herein are preferably high efficiency filters and can be selected from among several conventional devices, such as electrostatic precipitators, reverse gas fabric filters, and pulse jet fabric filters. A preferred arrangement includes the use of irradiation sources in an outlet manifold or duct carrying treated gas from the high efficiency particulate matter control system. Alternatively, irradiation can be performed within the electrostatic precipitator, reverse air fabric filter, or pulse jet fabric filter. The radiation beams are generally directed parallel to the direction of gas flow in the outlet manifold or in the high efficiency particulate matter control systems.

Conventional UV irradiating sources are employed. The radiation source may comprise any conventionally generated UV radiation. Radiation in a spectral range of 230 to 370 nanometers is preferred in Stage I and in the preferred spectral range of 230 to 370 nanometers in Stage II treatments, such as by lamps with arc emission such as xenon, mercury, or xenon-mercury, or with pulsed or continuous lasers. Other available sources of UV light may be used. The source of radiation may be located outside the

irradiation zones and emitted through sealed quartz windows protruding through the structural wall of the zones. Preferably, the source of radiation is located inside the photochemical reaction zone.

The number of UV emitting devices used in Stage I processing in the treatment of elevated ammonia gas can vary in relation to the heated gas flow rate, the residency time, and/or the concentration of ammonia and the concentration of organic compounds in the gas stream. A recommended intensity range is from 200 to 2,000 microwatts/cm$^2$ measured at 254 nanometers and 1,000 to 20,000 microwatts/cm$^2$ measured at 360 nanometers. Light absorption levels from 1 to 100 microwatts per exposed cubic feet of gas are effective in conversion of ammonia to lesser toxic byproducts. Excessive irradiation levels could form free radical byproducts from ammonia and the co-present organic compounds, which are preferably minimized by establishing the optimum UV light treatment conditions, e.g., gas volume, temperature, organic compounds concentrations, and residency time estimated or measured in the irradiating zones. The residence time of gas in Stage I can vary. In one embodiment of the process, the residence time would be approximately 0.5 to 12 seconds. To ensure that the formation of undesirable byproducts are avoided, it is preferable that the light intensity and residence time be limited to avoid a reduction of more than 50% of the $NO_x$ (total of NO and $NO_2$) and to avoid a $NO_2$/NO ratio of greater than 10.

The ammonia gas that is not destroyed in the adsorption step of Stage I remains in the effluent gas stream, which is directed through the high efficiency particulate matter control device. The gas phase ammonia in the effluent gas stream exiting the particulate matter control device is exposed to UV radiation in the spectral range of 230

to 370 nanometers to photochemically oxidize the ammonia. The direct photolytic oxidation of ammonia remaining in the effluent gas stream from the particulate matter control device is termed Stage II control.

The Stage II photoreactor, generally comprises a manifold or duct leading from the high efficiency particulate matter control device or a structural housing that surrounds and/or supports a high efficiency particulate removal treatment zone.

Referring to Figure 1, wherein like numerals depict like features or components, there is shown therein a multi-stage system that comprises a fossil fuel, wood fuel, or waste fuel fired boiler **1** handling hot combustion gases generated in the flames of burners **2** mounted in boiler **1** and combusting fuel and air directed to the burners. The fuel and air can be received at burners **2** as pulverized solid material, liquids, or solids having size ranges from 100 micrometers to more than 4 inches diameter. Hot combustion gases formed due to the combustion of the fuel and air are formed and moved upward in the refractory lined combustion chamber that comprise the walls of boiler **1**. The hot combustion gases containing nitrogen oxides, organic compounds, and particulate matter are exposed to a spray of ammonia or urea from one or more sets of nozzles **4** mounted in an area of the boiler **1** where the gases are in the temperature range of 1600°F to 2000°F. The ammonia or urea spray **4** that is part of the SNCR system results in the chemical reduction of $NO_x$ to $N_2$ and the typical formation of 2 ppm to 40 ppm ammonia gas in the combustion gas stream exiting the combustion zone of the boiler **1**.

The hot ammonia-containing gases are treated in a series of heat exchangers **6** such as superheaters, reheaters, and feed water economizers to recover sensible heat

and, thereby, reduce the gas temperature to the range of 500°F to 1,000°F. The effluent gas stream from the heat exchange equipment **6** is then exposed in some industrial processes to ammonia spray **9** that is part of the SCR system. The ammonia gas introduced from ammonia spray nozzles **9** reacts with $NO_x$ remaining in the gas stream on the surface of catalyst beds **10**. The resulting combustion gas stream exiting the catalyst beds **10** has substantially reduced $NO_x$, approximately 2 ppm to 40 ppm ammonia, organic compounds, and particulate matter.

A series of UV lights or lamps **11** are mounted in or are protruding through the walls of a lamp housing **12** mounted around or adjacent the downstream catalyst bed **10**. This set of lamps is termed Stage I. In one embodiment, lights **11** are oriented to irradiate the gas as it enters, passes through, and exits the last SCR catalyst bed. Disposed around the lights **11** is the lamp housing **12** for mounting and cooling the lights **11**. Air having a temperature that provides cooling, such as ambient air or air recycled from a portion of a gas stream is directed through the lamp housing **12** to maintain the temperature surrounding the lamps **11**.

The combustion gas stream exiting the Stage I treatment area is directed to one or more heat exchangers **14** to remove sensible heat from the combustion gases. These heat exchanger can include feed water economizers and air preheaters. The cooled combustion gas stream then enters a high efficiency particulate matter control system **16** such as an electrostatic precipitator, reverse air fabric filter, or pulse jet fabric filter. Combustion gases with the substantially reduced particulate matter concentration enter an outlet manifold or duct **18** to transport the treated gas stream to a fan **23** and stack **24**.

With reference to figure 1, Stage II control includes a set of UV lamps **19** and a lamp housing **20.** Additionally, cooling air can be directed through the housing **20** to cool the UV lamps **19**. In Stage II, the frequency of radiation of the filtered gas should be in a range of from 230 to 370 nanometers, preferably from 250 to 320 nanometers. The lamps **19** should have an intensity selected so as to provide about 200 to 2,000 microwatts/cm$^2$ measured at 254 nanometers and 1,000 to 10,000 microwatts/cm$^2$ measured at 360 nanometers resulting in light absorption levels of from 1 to 100 microwatts per cubic feet of irradiated gas. A recommended residency time for Stage II irradiation is approximately 0.5 to 12 seconds. This residency time and irradiation intensity are preferably limited to the extent necessary to ensure that no more than 50% of the inlet $NO_x$ is lost and that the $NO_2/NO$ ratio following photochemical free radical chain reaction treatment does not exceed 10. Alternatively, the UV lamps can be provided within the high efficiency particulate matter control device and oriented to direct the irradiation beam with a maximum path length. The temperature of irradiated gas passing underneath the lamps **19** can be held in a range of from 200°F to 700°F and is preferably maintained in a range of from 200°F to 400°F. These temperature ranges can be varied from the above suggested range and yet provide effective treatment of gas, depending on factors that will be apparent to one of ordinary skill given the compositional and process parameters actually encountered.

Connected to the outlet manifold or duct **18** is an outlet duct **22** that junctions to the fan **23** that is operative to expel and direct the filtered, irradiated gas stream into stack **24**. As an option, there could be provided a series of UV lights associated with the stack **24** and operating in a spectral range above 230 nanometers. This set of

stack mounted lights would continue the photolytic destruction of ammonia that occurs naturally due to sunlight when the gas stream is expelled from the stack.

It is contemplated that the lamps or lights **19** are advantageously selected so as to provide an intensity of 200 to 2,000 microwatts per square centimeter measured at 254 nanometers and 1,000 to 20,000 microwatts per square centimeter measured at 360 nanometers and thereby result in light absorption levels of 1 to 100 microwatts per actual cubic foot of gas treated. It is appreciated and within the spirit and scope of the invention to establish operable settings of light intensity to avoid the formation of photochemical free radical reaction byproducts. The formation of undesirable byproducts is avoided by controlling light intensity and/or irradiation time to the extent necessary to avoid converting more than 50% of the total inlet $NO_x$ to compounds other than NO and $NO_2$ and by keeping the $NO_2$/NO concentration ratio at values less than 10. In a typical process, it is contemplated that the $NO_x$ concentration maintained in the gas stream being treated would be on the order of 50 to 300 ppm. This should be sufficient to maintain an active set of free radical chain reactions.

The residency time in the outlet manifold or duct **18** can be varied, but under typical conditions encountered, the residency time of the gas stream is approximately 0.5 to 12 seconds. It may be desirable to limit the residence time in the irradiation chamber to avoid the formation of photochemical-free radical reaction by products.

The chemical reactions involved in Stage I and Stage II are identical and are summarized below. It is understood that these reactions are provided only to illustrate the operation of the process and do not include all of the hundreds to thousands of free

radical reactions initiated in high temperature, high gas concentration photochemically initiated free radical chain reactions.

The principal reactions providing for the removal of ammonia include irradiating the gas stream and through irradiation, disassociating hydrogen atoms from the ammonia to form $NH_2$. Thereafter reacting the $NH_2$ with NO or $NO_x$ to form nitrogen gas and/or water. Some of the disassociated hydrogen atoms form $H_2O$. Other disassociated hydrogen atoms form hydroperoxy ($HO_2$) free radicals that continue to initiate oxidation reactions with the ammonia. More particularly, the hydroperoxy free radicals react with ammonia and effectively pull a hydrogen atom from the ammonia molecule.

**STAGE I and STAGE II REACTIONS**

Principal Ammonia Reactions

| | | | |
|---|---|---|---|
| $NH_3 + OH\bullet$` | $\rightarrow$ | $NH_2\bullet + H_2O$ | Reaction 1 |
| $NH_3 + HO_2\bullet$ | $\rightarrow$ | $NH_2\bullet + H_2O_2$ | Reaction 2 |
| $NH_3 + HO_2\bullet$ | $\rightarrow$ | $NH_2\bullet + 2OH\bullet$ | Reaction 3 |
| $NH_2\bullet + NO$ | $\rightarrow$ | $N_2 + H_2O$ | Reaction 4 |

Principal Photolysis Reactions

| | |
|---|---|
| $NO_2 + h\nu$ (270 - 370 nanometers) $O(^3P)\bullet + NO$ | Reaction 5 |
| $O3 + NO \rightarrow NO_2 + O_2$ | Reaction 6 |
| $O_3 + h\nu$ (250-306 nanometers) $\rightarrow O(^1D)\bullet + O_2(\Delta_g)$ | Reaction 7 |
| $H_2O_2 + h\nu$ (<370 nanometers) $\rightarrow$ $2HO\bullet$ | Reaction 8 |

| | | | |
|---|---|---|---|
| $RCHO + h\nu$ (<370 nanometers)$\rightarrow R\bullet + CHO\bullet$ | | | Reaction 9 |
| $N_2O_4 + h\nu$ (250-310 nanometers) | | $NO + NO_2 + O(^3P)\bullet$ | Reaction 10 |

<u>Principal Free Radical Reactions</u>

| | | | |
|---|---|---|---|
| $H\bullet + O_2$ | $\rightarrow$ | $HO_2\bullet$ | Reaction 11 |
| $O(^3 P)\bullet + O_2$ | $\rightarrow$ | $O_3$ | Reaction 12 |
| $O(^1D) + H_2O$ | $\rightarrow$ | $2HO\bullet$ | Reaction 13 |
| $O(^1D)\bullet + H_2O$ | $\rightarrow$ | $O(^3P)\bullet + H_2O$ | Reaction 14 |
| $HO\bullet + CO$ | $\rightarrow$ | $H\bullet + CO_2$ | Reaction 15 |
| $H\bullet + O_2$ | $\rightarrow$ | $HO_2\bullet$ | Reaction 16 |
| $HO_2\bullet + NO$ | $\rightarrow$ | $HO\bullet + NO_2$ | Reaction 17 |
| $O_3 + RHC{=}CHR$ | $\rightarrow$ | $RCHO_2\bullet + RCHO$ | Reaction 18 |
| $RO_2\bullet + NO$ | $\rightarrow$ | $RO\bullet + NO_2$ | Reaction 19 |
| $R\bullet + O_2\ (+M)$ | $\rightarrow$ | $RO_2\bullet\ (+M)$ | Reaction 20 |
| $HO\bullet + RH$ | $\rightarrow$ | $H_2O + R\bullet$ | Reaction 21 |

Where: M = Third body molecule, R = Alkyl substituted group (ie. H, $CH_3$)

These reactions collectively result in a predictable pattern to NO, $NO_2$, ammonia, $O_3$, and byproduct concentration profiles. These concentration profiles existing in the photochemical process equipment are similar to the concentration profiles observed over much longer time periods in polluted air undergoing smog reactions. As indicated in Figure 3, as the irradiation time proceeds, NO is first converted to $NO_2$ due to a variety of reactions, especially 6 and 17. NO2 photolysis is due to UV absorption. Carbon monoxide, water vapor, and hydrocarbons participate in this free radical chain

reaction by creating additional $HO_2$ and $RO_2$ free radicals that can convert NO to $NO_2$. During this time, hydroxy (OH) and $HO_2$ free radicals are available to remove a hydrogen atom from ammonia as indicated in Reactions 1, 2, and 3. During the time that NO and $NO_2$ are present in abundance, the formation of undesirable byproducts such as ozone and nitrates is avoided. However, after irradiation proceeds beyond the peak in the $NO_2$ concentration curve, the free radical chain reactions can result in the formation of these byproducts. Accordingly, the irradition time and/or intensity must be minimized to avoid free radical chain reactions beyond the $NO_2$ peak. This peak is indicated by $NO_2$/NO concentrations ratios in excess of 10 and by a total NO + $NO_2$ concentration that is less than 50% of the initial NO + $NO_2$ concentration.

The process described above for reducing or minimizing ammonia gas in an industrial gas stream can be applied to many industrial processes either with or without SNCR or SCR $NO_x$ control systems. One particular application of the present process and system is to cement manufacturing facilities that, in some case, have a tendency to form ammonia gas due to the thermal breakdown and reactions of organic nitrogeneous compounds such as amines present in low concentrations in the limestone feed to the kilns. The thermal reactions of the kiln feed can result in the formation of ammonia gas in the concentration range of 2 ppm to 250 ppm.

The components of a conventional cement or portland cement manufacturing facility relevant to the invention are depicted in Figure 2, which is a schematic illustration of effluent streams downstream of a kiln. Aspects of a conventional cement manufacturing facility (not illustrated) are well known and are beyond the scope of this disclosure. A cement manufacturing facility typically comprises a

pyroprocessing system including a rotary kiln **102** having a burner **105** disposed in the outlet end thereof, and a preheater tower. In the preheater tower, there is included a series of cyclones, such as illustrated at **106** and **108**.

In conventional fashion, a gas stream is generated in the kiln **102**. The gas stream moves from the kiln **102** through a gas duct **110** to the lower cyclone **108**. Gas entering cyclone **108** may be directed through portions of the cyclone and ultimately exits the cyclone **108** via duct **112**. Duct **112** leads to the second cyclone **106**. The gas stream enters cyclone **106** via duct **112** and is, in conventional fashion, directed to various areas within the cyclone. Ultimately, the gas stream exits cyclone **106** and enters main duct **130** that ultimately leads from cyclone **106** to a fan **132**. An alkali bypass stream **160** is formed by withdrawing a portion of the main effluent gas stream exiting the kiln **102**. This alkali bypass stream is typically treated in a separate gas cooling tower **161** and a high efficiency particulate matter control device **162**. A fan **163** pulls the alkali bypass stream from the particulate matter control device **162** to a stack **164**. The purpose of the alkali bypass stream is to relieve the system of sodium, potassium, sulfates, and/or chlorides.

Cyclones **106** and **108** are adapted to receive a conventional raw feed, typically limestone, and in some cases, additives such as clay and sand. The raw feed is typically directed through a feed line **114** into duct **112** carrying the gas stream from cyclone **108** to cyclone **106**. The raw feed entering duct **112** mixes with the gas stream and is directed into cyclone **106** and gravitates downward through cyclone **106** while being preheated. The raw feed exits cyclone **106** through feed line **116**. Figure 2 depicts feed a line **116** that joins the gas stream duct **110**. There, the raw feed

mixes with the gas stream traveling in duct **110** and be directed into the lower cyclone, cyclone **108**. Once in cyclone **108**, the raw feed gravitates downward through the cyclone and, in the process, is preheated therein. Ultimately, the preheated raw feed exits cyclone **108** into feed line **118** that carries the preheated raw feed to kiln **102**. In kiln **102**, the raw feed is subjected to heating to approximately 2,800°F and, during this course, cement clinker is produced, which is directed out the output end of kiln **102**. The gas stream exiting cyclone **106** is directed into duct structure **130** that leads from the cyclone **106** ultimately to fan **132**.

It is appreciated that there are numerous variations among the basic components of a cement manufacturing facility. For example, there can be any number of cyclones that form a part of the pyroprocessing system of a cement plant. In addition, and in the way of an example, some cement manufacturing plants do not include preheaters. The ammonia destruction process herein is readily adapted to destroying ammonia in preheater, preheater-precalciner, long dry, and wet type portland cement plants. Accordingly, the illustration discussed above and shown in Figure 2 is principally for explanation purposes.

Disposed between cyclone **106** and fan **132** is a photochemical reactor indicated generally by the numeral **120**. Reactor **120** includes a housing or duct structure **122** through which a gas stream passes, that is the gas stream moving from cyclone **106** to fan **132**. Within the reactor **120** there is provided a series of UV lamps **124**. Reactor **120** functions to remove ammonia from the gas stream passing therethrough in much the same manner as described in the Stage I process discussed with respect to Figure 1.

It is contemplated that the lights **124** used in the reactor **120** would radiate light within a spectral range of 230 to 370 nanometers. This would entail UV light. The number of lights **124** used in reactor **120** could vary based upon the flow rate of the gas stream, the chemical make-up of the gas stream and other factors. However, it is contemplated that the lamps **124** would be selected so as to provide an intensity of 200 to 2,000 microwatts per square centimeter measured at 254 nanometers and 1,000 to 20,000 microwatts per square centimeter measured at 360 nanometers and, thereby, result in light absorption levels of 1 to 100 microwatts per actual cubic foot of gas treated. The light emitted by the lamps **124** in the the spectral range fo 230 to 370 nanometers would be absorbed by nitrogen oxides and organic compounds and would typically result in the formation of hydroxy and hydroperoxy radicals. These hydroxy and hydroperoxy radicals react with ammonia to yield the $NH_2$ radical that reacts further to yield $N_2$. It should be noted that the light intensity is preferably limited to avoid the formation of photochemical free radical reaction byproducts.

The gas stream exiting the fan **132** is directed to a high efficiency particulate matter filter chamber **140** similar to the chamber **16** shown in Figure 1. After the gas stream has passed through the high efficiency particulate control systems, the filtered gas stream is exposed to another series of lights or lamps **150**. This is essentially Stage II treatment. Details of the particulars for Stage II treatment will not be repeated here as they are essentially the same as discussed above with respect to Stage II and as shown in Figure 1. However, Stage II would typically include lamps **150** having a spectral range of 230 to 370 nanometers. Like in the process discussed above and shown in Figure 1, Stage II treatment in the case of the cement manufacturing facilty

focuses on the gas stream after particulate matter has been removed by a filtering process.

From Stage II, as shown in Figure 2, the gas stream is directed through line **152** to a fan **154** that directs the gas stream to a stack **156**.

## EMPIRICAL STUDY OF THE AMMONIA REDUCION BY TREATMENT OF UV RADIATION

An empirical study of the photochemical reduction of ammonia has been performed. A gas composition was produced to simulate a typical cement manufacturing industrial gas stream. A gas stream consisting of ammonia, nitric oxide, carbon monoxide, organic compounds, and air was treated with UV radiation. Ammonia concentrations were measured by a continuous emissions monitoring system with and without UV radiation treatment to determine reduction efficiency. The light spectra included 230 to 370 nanometers, and the light intensity was varied to establish a reduction efficiency range. A sample of the results are provided in Table 1.

Table 1. Photochemical Reduction Results

| Ammonia[1] (ppm) | NO (ppm) | Acetone (ppm) | CO (ppm) | $O_2$ (%) | Gas Flow Rate (l/min) | Residence Time (Seconds) | Reduction Efficiency (%) |
|---|---|---|---|---|---|---|---|
| 114 | 266 | 15 | 113 | 12.4 | 2 | 26 | 47 |
| 28 | 437 | 28 | 258 | 8.3 | 1.8 | 20 | 90 |
| 28 | 400 | 23 | 212 | 7.2 | 2.4 | 8.5 | 47 |
| 21 | 460 | 22 | 200 | 7.0 | 4.3 | 5 | 20 |

[1] Untreated concentration